Role of Water Structure & Its Alteration by Various Electrolytes in Heavy Water Production

D. G. PRADHAN

Heavy Water Project (Talcher), Talcher Fertilizer Township
Dhenkanal, Orissa 759131

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The role of water structure and its alteration by various solutes such as quinoline hydrochloride, 8-nitroquinoline, 8-hydroxyquinoline hydrochloride and 2-methylquinoline have been studied with a view to developing a method for heavy water production. 8-Hydroxyquinoline hydrochloride and 2-methylquinoline hydrochloride enrich the deuterium content in the first fraction of distillate and hence have been termed as structure-making solutes. 8-Nitroquinoline hydrochloride causes reduction in the deuterium content in the first fraction and hence has been termed as structure-breaking. Quinoline hydrochloride has marginal structure-breaking property. This difference in the behaviour of the organic bases is attributed to the differences in the charge density on nitrogen atom due to the presence of electron withdrawing or electron donating groups.

IN the present investigation, an attempt has been made to show the feasibility of improving heavy water production by distillation and electrolysis of water using electrolytes having structure-breaking and structure-making properties. Some experiments have also been carried out with known structure-making species. The observation[1] that the initial portions of water removed from compounds containing coordinated water gets enriched in heavy water has been examined in the light of residence time of ionic hydration[2]. A general theory for structure-making and structure-breaking properties of solutes in water has been put forward based on the deuterium content of the first fraction of the distillate.

Distilled water with deuterium content of 153·5 ppm was used for preparing all the solutions. Urea (LR, M & B), 8-hydroxyquinoline (AR, BDH) and 8-nitroquinoline (AG, Fluka) were used without further purification. Quinoline, 2-methylquinoline and N,N-dimethyl-1-*p*-toluidine were distilled before use. Hydrochlorides of the organic bases were prepared according to the literature procedure[3] and dried under vacuum. Some of the hydrochlorides were very hygroscopic and dry box was needed for handling them. No hydrolysis correction has been made for the hydrochlorides of organic bases as such a correction was found[3] unnecessary for the determination of apparent molal volumes of the substituted pyridinium chlorides in water under the concentration range used in the present investigation.

50 ml of the solution of each compound were taken in a flat-bottomed flask connected to a manometer and vacuum pump through a trap cooled by dry ice. The flask was kept in a thermostat and the solution stirred. All experiments were carried out at $30° \pm 0·01°$. Initial water samples from each solution were collected under constant reduced pressure for a specific time interval and the deuterium content of each water sample analysed using a Thompson-CSF, TSN 202B mass spectrometer with an accuracy of $\pm 0·2\%$ (relative). It was not always sufficient to know the deuterium content of initial water samples only as compounds containing exchangeable hydrogen atoms, when used in high concentration, may deplete the deuterium content of water if the deuterium content of the compound is lower than that of the water. In such cases deuterium content of the final fraction has also to be analysed as it has been done[1] in case of urea, $(NH_4).2SO_4$, etc. Experiment with $Fe(NO_3)_3.9H_2O$ (AR, E. Merck) was carried out as reported[1] earlier.

Urey has suggested[4] that a good method of concentration of heavy water by distillation of water is to use an aqueous solution of water-containing complexes if the fractionation factor is substantially larger than it is in water. The first layer of water molecules around an ion is ordered or structured and water molecules in the second hydration shell are more mobile than in pure water and hence this region is known as the region of structure-breaking. Beyond this water is structurally normal.

The difference in deuterium content of the water distillates collected from solutions of various compounds at different concentrations (Table 1) can be explained on the basis of structure-making and structure-breaking effects of the solutes. It has been observed[1] that removal of HDO molecules is easier compared to removal of H_2O molecules from compounds containing coordinated water because of the relatively lower nucleophilicity of the former. Therefore, compounds which enrich the deuterium content of the distillate samples can be said to exert a net structure-making effect while compounds which cause a reduction in the deuterium content of the distillate (as compared to distilled water) can be said to exert a net structure-breaking effect. Such effects are observed in the presence of high concentrations of the compounds. Water structure alteration has, however, been reported[3] to occur with very low concentrations of the hydrochlorides of substituted pyridines. Similar effects have been obtained in the present investigation with low concentrations of hydrochlorides of quinoline and sub-

TABLE 1 — DEUTERIUM CONTENT IN THE FIRST FRACTION OF DISTILLATE OF THE SOLUTION OF VARIOUS COMPOUNDS AT DIFFERENT CONCENTRATIONS

Compound	Concentration	Deuterium content (ppm)
Distilled water*	—	150·6
Urea*	Saturated	142·4
Quinoline hydrochloride	0·2*M*	148·9
8-Nitroquinoline hydrochloride	0·2*M*	143·0
8-Hydroxyquinoline hydrochloride	0·1*M*	154·1
8-Hydroxyquinoline hydrochloride	0·2*M*	156·8
2-Methylquinoline hydrochloride	0·2*M*	162·7
N,N-Dimethyl-*p*-toluidine hydrochloride	0·2*M*	150·3

*From reference 1.

stituted quinolines. This observation is interesting in that a quantitative correlation between the forces responsible for the alteration of water structure can be found out using these hydrochlorides. It should be realized that nitrogen positive centres and their stabilization by various factors are of primary importance in water structure alterations[3]. The hydroxy group in 8-hydroxyquinoline hydrochloride may reduce the charge density on nitrogen compared to quinoline hydrochloride and thereby reduce the structure-breaking ability of the nitrogen positive centre so much so that it eventually becomes structure-making. The marginal structure-breaking effect of quinoline hydrochloride should be noted (a difference of 1·7 ppm only, Table 1). The above fact is supported from the experiment with 8-nitroquinoline hydrochloride wherein an enhanced structure-breaking effect is observed due to the resonance stabilized increase in charge density on nitrogen by the electron withdrawing nitro group. Apart from this electronic effect a steric effect is indicated from the enhanced structure-making effect of the hydrochloride of 2-methylquinoline. Similar structure-making effect has been reported[3] for 2,6-dimethylpyridinium chloride and bromide.

The experiment with N,N-dimethyl-*p*-toluidine hydrochloride is interesting as it is not altering the structure of water. It contains sp^3-hybridized nitrogen and thus does not become structure-making in spite of it having three methyl groups.

Hydration of ions in aqueous solutions is generally characterized by the hydration number. However, there is always a possibility of exchange between the closest molecules of water in an aqueous solution and hence the residence time of ionic hydration has been described[2] to be more appropriate for characterizing hydration of ions. Residence time depends on the quantity ΔE_i which is the difference between the energy required by a water molecule to escape from the immediate neighbourhood of the ion and the energy in free water of aqueous solution required for a water molecule to replace its neighbour. In cases for which $\Delta E_i > 0$, termed positive hydration, exhange of nearest water molecules is not frequent. Cases for which $\Delta E_i < 0$ are termed negative hydration. Positive hydration alone is not enough to cause a given ion to move with its hydration shell. Strong hydration with large positive ΔE_i is necessary for such a movement. Extreme cases for such structure-making ions can be said to be present in crystalline hydrates containing coordinated water molecules. While removing this coordinated water by distillation, heavy water comes out first due to the reasons described earlier[1]. The deuterium content of the first two fractions of water removed from 500 g of crystalline $Fe(NO_3)_3.9H_2O$ has been found to be 232·6 and 213·0 ppm respectively. Selective excitation with infrared light of wavenumber 1455 cm^{-1}, for example, would reduce the nucleophilicity of HDO molecule further and facilitate its removal.

It can be concluded that in the cases of strong hydration (large positive ΔE_i) where the entire hydration complexes are altered and in extreme cases of solutions of structure-making salts such as crystalline hydrates containing coordinated water, heavy water is removed easily compared to light water. This offers a new method for the enrichment and production of heavy water[1]. On the other hand, ions whose residence time of hydration is small and ΔE_i is negative, less of heavy water will come in the initial fractions when used in appropriate concentration. Here again it is the major role of the structure of water and its destruction by structure-breaking solutes that makes the development of negative hydration feasible which can be utilized to improve heavy water production by electrolysis and distillation. Urea has been found[1-5] to be a suitable structure-breaking species.

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Computation of Deuterium Isotope Effect in Metal Hexaammine-Ammonia Exchange Process

R. R. SINGH & D. G. PRADHAN

Heavy Water Project (Talcher), Talcher Fertilizer Township Dhenkanal, Orissa 759131

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Several metal hexaammine complex-ammonia exchange systems have been examined for equilibrium isotope effect and equilibrium constants, and separation factors have been calculated from the normal modes of vibrations. The results indicate suitability of $Ni(NH_3)_6^{2+}$-ammonia system for large-scale deuterium enrichment. The magnitude of the isotope effect is shown to be dependent on the harmonicity of the N-H bond vibrations.

THE ammonia exchange in some metal hexaamine complex-ammonia systems is very rapid[1] and is, therefore, a suitable reaction for the deuterium enrichment by exchange process provided the equilibrium constants are high enough for deuterium-protium separation to take place appreciably. To determine the extent of isotope separation, an investigation has been carried out to calculate deuterium isotope effect in such systems by the methods of Bigeleisen and Mayer[2] and Urey[3] using the best available data on the vibrational frequencies. The